THE STRUCTURE OF THE CHLORITES

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By the application of the same methods of investigation as those used in the study of the micas,[1] I have determined the structure of the chlorites, a group of minerals morphologically similar but distinctly different in chemical composition. This structure is described in the following paragraphs.

Data obtained from oscillation and Laue photographs of specimens of penninite and clinochlore, of composition approximating the formula $Al_2Mg_5Si_3O_{16}(OH)_8$, lead to a monoclinic unit of structure with a = 5.2–5.3 Å., b = 9.2–9.3 Å., c = 14.3–14.4 Å., $\beta = 96°50'$, containing two molecules as written above. The lattice is apparently end-centered on (001), the space group being C_{2h}^3.

The close approximation of the values of a and b to those for the micas indicates that these crystals, too, are composed of tetrahedral and octahedral layers. The composition requires that in unit length along c there be two tetrahedral layers and two complete octahedral layers such as in brucite. Now we expect that as a rule the two faces of a constituent layer of a layer crystal will be equivalent, for if they were not equivalent there would be a tendency for the layer to curve, one face becoming concave and one convex, and this tendency would in general not be overcome by the relatively weak forces operative between adjacent layers. This symmetry is possessed by the layers of nearly all known layer structures—the micas, brittle micas, etc., brucite, hydrargillite, cadmium chloride, molybdenite and the A-modification of the sesquioxides. It is probable that kaolinite, $Al_2Si_2O_5(OH)_4$, is an exception. The very close approximation in dimensions of the octahedral layer in hydrargillite, $Al(OH)_3$, with b = 5.07 Å., a = 8.65 Å., and a complete layer of silicon tetrahedra, with a = 5.03 Å., b = 8.71 Å. (as in β-tridymite and β-cristobalite), shows that an unsymmetrical layer composed of these two, as in figure 1, would have only a very small tendency to curve, which could be overcome by the forces between layers. This structure for kaolinite (the different modifications of which would differ in the method of superposition of the layers) is supported by Hendrick's observation[2] that the value of d_{001} is about 7.1 Å., in agreement with prediction.

The non-existence of a magnesium analogue of kaolinite is accounted for by the large values of the fundamental translations in the brucite layer (with a = 5.40 Å.), which would cause the kaolinite-type layer to curve.

The chlorites are composed of mica layers and brucite layers alternating,

as shown in figure 2. Each of these layers is symmetrical. Aluminum tetrahedra expand the tetrahedral layers enough to allow them to be comfortably fitted on to a complete octahedral layer, as in biotite. The substitution of Al^{+3} for Si^{+4} gives the mica layers a resultant negative charge, as in the micas and brittle micas themselves. This is compensated by the alternating brucite layers, each of which through the sub-

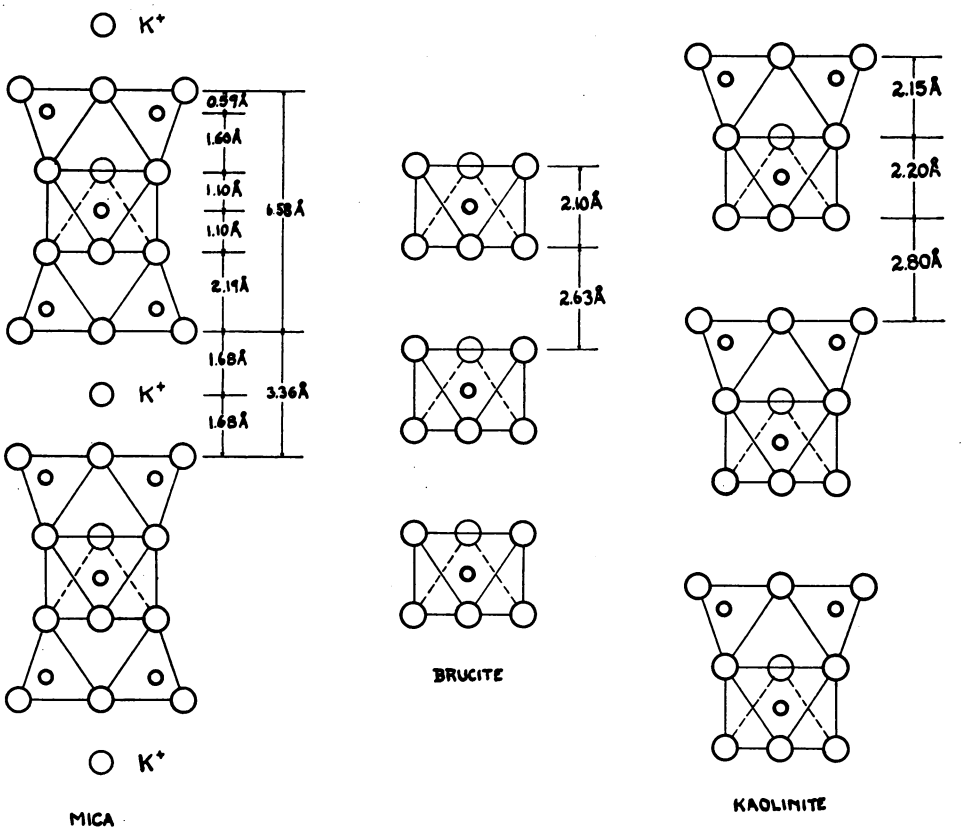

FIGURE 1

The structures of mica, brucite and kaolinite, showing the sequence of atom layers normal to the cleavage planes. Large circles represent O^- or OH^- (or K^+ when so marked), small ones Si^{+4} or Al^{+3} (at tetrahedron centers) and Mg^{++} or Al^{+3} (at octahedron centers). In each layer the atoms are arranged as described in Ref. 1.

stitution of Al^{+3} for Mg^{++} has a resultant positive charge, and which play the same rôle as K^+ and Ca^{++} in the micas and brittle micas.

Assuming that all the atoms in a layer have the same z coördinate, the succession of atoms normal to (001) is given by four parameters, with the predicted values $z_1 = 0.080$, $z_2 = 0.230$, $z_3 = 0.425$, and $u = 0.190$. The relative intensities of reflection in various orders from (001) are then determined by the amplitudes

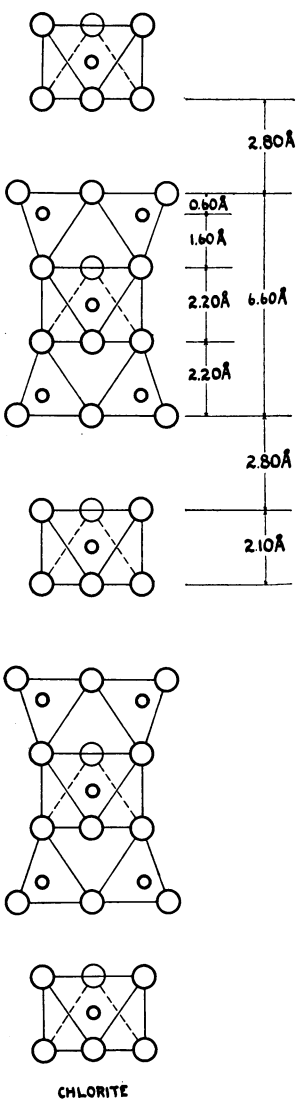

FIGURE 2

The sequence of atom layers normal to the cleavage plane of chlorite, showing mica layers of composition varying between $[Mg_3AlSi_3O_{10}\ (OH)_2]^-$ and $[Mg_3Al\ Al_2Si_2O_{10}\ (OH)_2]^-$, alternating with charged brucite layers, $[Mg_2Al(OH)_6]^+$.

$$A_{001} = 6A_{Mg,Al}\{1 + (-1)^l\} + 8A_{Si,Al}\cos 2\pi lu + 12A_O\{\cos 2\pi lz_1 + \cos 2\pi lz_2 + \cos 2\pi lz_3\}.$$

In table 1 are given values of $A^2/1600$ calculated in this way, together with the observed relative intensities of reflection in 26 orders from (001), obtained by the visual comparison of four photographs (made using MoK_α radiation) taken under identical conditions except for exposure times ranging from $8^1/_2$ min. to 1050 min. The comparison is shown graphically in figure 3. The agreement is excellent, verifying the suggested structure. The agreement is deleteriously affected by changing any of the parameters by as much as 0.01 from its predicted value.

The structure leads to the general chemical formula $X_mY_4O_{10}(OH)_8$, with $4 \leq m \leq 6$.

Actually m is equal to 6 for the great majority of the chlorites, which then contain complete octahedral layers only. With $m = 4$ the crystal would have the same composition as kaolinite; it is probable, however, that the kaolinite structure described above is the more stable, and that this lower limit for m is never closely approached. The constituent Y_4, ions with the coördination number 4, varies within the range between Si_3Al (as in penninite and clinochlore) and Si_2Al_2 (in amesite). The latter limit is imposed by the electrostatic valence rule; beyond it there would be some oxygen ions with the too low value $1^1/_2$ for Σs. With $m = 6$ the constituent X_m, ions with the coördination number 6, varies between Mg_5Al and Mg_4Al_2, with Fe^{++} and Mn^{++} sometimes partially replacing Mg^{++} and Fe^{+3} replacing Al^{+3}.

The existence of hexagonal layers of tetrahedra and octahedra in the chlorites accounts for their pronounced pseudohexagonal nature. The presence of layers not held together by anion-cation contacts explains their excellent cleavage on (001). The chlorites are not so soft

as kaolinite and talc because of the fact that the layers are charged alternatively positive and negative. On the other hand, the cleavage lamellae, while tough, are not elastic as in the micas, for the effect of the potassium ions in the micas in keying adjacent layers is here absent. The presence of

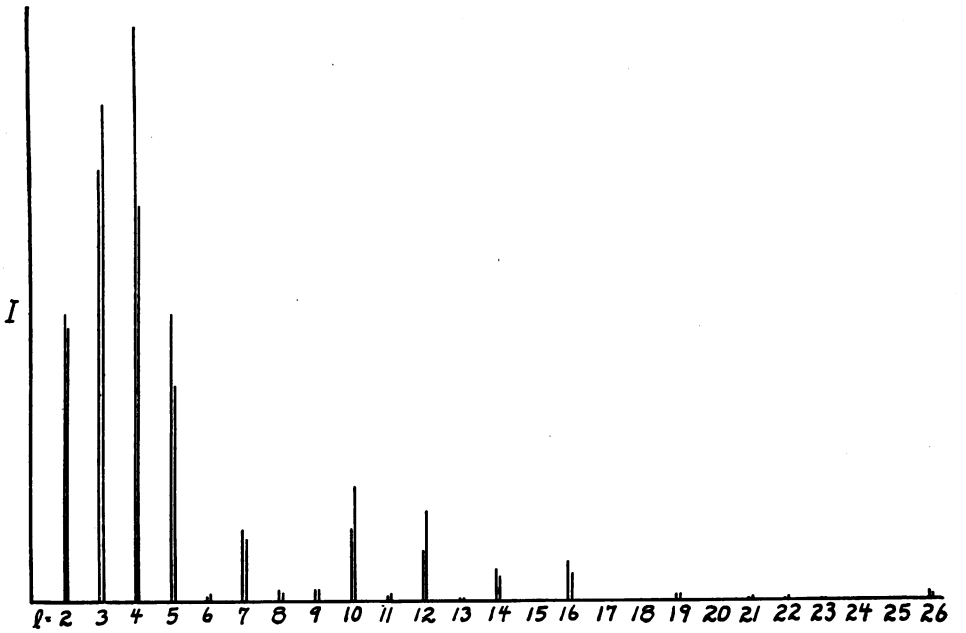

FIGURE 3

Comparison of the observed and calculated intensities of reflection of X-rays from (001) of penninite, in the 2nd. to 26th. order. Of each pair of vertical lines that on the left shows the observed intensity, that on the right the calculated intensity.

mica layers accounts for the possession by the chlorites of the same percussion and pressure figures as the micas, and also for the fact that chlorites and micas often form parallel growths and that the micas (particularly biotite) are easily altered into chlorites.

TABLE 1

OBSERVED AND CALCULATED INTENSITIES OF REFLECTION FROM (001) OF PENNINITE

Order of reflection	1	2	3	4	5	6	7	8	9	10	11	12	13
Observed intensity	4*	40	60	80	40	0.5	10	1.5	1.5	10	0.5	7	0.2
Calculated intensity	37	38	69	55	30	0.9	8.4	0.9	1.5	16	0.9	12.5	0.3
Order of reflection	14	15	16	17	18	19	20	21	22	23	24	25	26
Observed intensity	4.5	0.0	6	0.0	0.0	0.8	0.0	0.2	0.1	0.0	0.0	0.0	1
Calculated intensity	3.4	0.0	3.9	0.1	0.0	0.8	0.1	0.5	0.8	0.0	0.0	0.0	0.7

* The experimental arrangement used was such as to make the first order reflection abnormally weak.

It is evident that further crystals containing mica and brucite layers might exist. Representing a mica layer by M^-, a charged brucite layer by B^+ and a layer of potassium ions by K^+, the succession of structures

Mica:	$M^- K^+ M^- K^+ M^- K^+ M^- K^+$
Intermediate:	$M^- K^+ M^- B^+ M^- K^+ M^- B^+$
Chlorite:	$M^- B^+ M^- B^+ M^- B^+ M^- B^+$

indicates how intermediates between mica and chlorite might be formed. Giving M^- and B^+ the representative compositions $[Mg_3AlSi_3O_{10}(OH)_2]^-$ and $[Mg_2Al(OH)_6]^+$, the intermediate shown would have the composition $KMg_8Al_3Si_6O_{20}(OH)_{10}$, and would have an effective interplanar distance on (001) of 24.3 Å., just the sum of those for mica and chlorite. Chlorite-brucite intermediates would probably be unstable because of the juxtaposition of two positively charged brucite layers.

A detailed account of this investigation will be published in the *Zeitschrift für Kristallographie.*

[1] Linus Pauling, These PROCEEDINGS, **16**, 123–129 (1930).
[2] S. B. Hendricks, *Zeit. Kristallographie*, **71**, 269 (1929).

DISCUSSION OF VARIOUS TREATMENTS WHICH HAVE BEEN GIVEN TO THE NON-STATIC LINE ELEMENT FOR THE UNIVERSE

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§1. *Introduction.*—In several previous articles,[1,2,3] I have shown the possibility of deriving a non-static cosmological line element to agree with the relatively uniform distribution of matter observationally found in the universe, and of using this line element to account both for the annihilation of matter taking place throughout the universe, and for the red-shift in the light from the extra-galactic nebulæ. After the publication of the first of these articles, I learned from a conversation with Professor H. P. Robertson that he had previously published[4] a different derivation of the same general form of line element; more recently Professor de Sitter and Sir Arthur Eddington have both been kind enough to call my attention to the previous use of a non-static line element by Lemaitre,[5] and still more recently I have discovered the early treatment of non-static line elements by Friedman.[6]

The purpose of the present article is to discuss certain features in this earlier work which overlap the treatment which I have given. Some remarks will also be made concerning an article by Eddington[7] which